Growth and Vacuum Ultraviolet Scintillation Characteristics of Fluoride Single Crystals

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論 文 内 容 要 旨

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Chapter 1 Introduction

Radiation detectors, comprised of inorganic scintillator and photomultiplier tube (PMT), are widely used for medical imaging, security inspection, high energy physics and several industrial applications. Accompanying the advance in aforementioned applications, high performance radiation detectors are required and thus an extensive research on inorganic scintillators has been carried out in the last decades. However, the PMT-based detectors have potential limitation in spatial resolution and cost due to the size and cost of PMT. In contrast to the PMT-based radiation detectors, the micropattern gaseous detectors (MPGDs) are attractive radiation detectors because they can realize the large area detector with excellent spatial resolution in low cost. However, due to the poor detection efficiency for high energy photons, MPGDs are difficult to use in medical application such as PET or X-ray CT.

In order to compensate the detection efficiency, the combination of inorganic scintillator and MPGDs has been studied. The VUV-sensitive MPGDs such as multi-wire proportional counter (MWPC), microgap photomultiplier (MGPM) and micropixel chamber (μ-PIC) have been developed in last decades. On the other hand, BaF_2 and Nd^{3+} doped LaF_3 ($Nd:LaF_3$) were intensely studied as candidates of the scintillator which can emit photons in vacuum ultraviolet (VUV) region. However, the high-quality scintillation crystal, especially in VUV region, is hardly obtained because the scintillation properties tend to be critically degraded by slight contamination with unfavorable impurities. Therefore, the radiation imaging detectors comprised of VUV scintillator and MPGD have not been realized so far.

This thesis provides insights into several aspects of the VUV luminescent scintillator toward the realization of radiation detectors with MPGDs. An introduction of scintillator, its application and the principle of MPGD are discussed in the first chapter. Experimental procedures are treated in the second chapter. The first successful example of radiation imaging detector comprised of $Nd:LaF_3$ and MPGD is presented in the third chapter. The experimental results of material survey and scintillation characteristics of discovered $Nd:LiLuF_4$ are provided in the fourth chapter. The crystal growth and scintillation characteristics of large single crystal of $Nd:LuF_3$ are presented in the fifth chapter.

Chapter 2 Experimental procedure

The micro-pulling down (μ-PD) method is a rather fast and economic tool for single crystal growth compared to the conventional Czochralski or Bridgman growth techniques. It has been successfully used for the oxide single crystalline material investigation, and has adapted to fluoride crystals. In this thesis, the μ-PD method was employed for the screening of fluoride host crystals, dopant concentration and optimization of the growth parameters for new crystalline materials.

Bulk single crystals were grown in a Czochralski (Cz) furnace which is originally designed and built for the growth of fluoride crystals. The induction heater was driven by a radiofrequency generator. A high purity graphite crucible was used for crystal growth because of its high durability in the fluorine atmosphere at high temperature. The double crucible system was employed to suppress the uneven distribution of dopant concentration due to the segregation.

Though spectrometers for the UV-visible spectral region are commonly used, the spectrometer in VUV region is hardly obtained. The difficulty on the evaluation of VUV luminescence has been one of the barriers against the progress in this field. Therefore, I have developed a table-top spectrometer which can evaluate the spectroscopic characteristics in VUV-UV-visible region. The spectrometer is equipped with the vacuum tight sample chamber evacuated and purged with high purity nitrogen to avoid the loss of VUV photons due to the absorption by oxygen. The X-ray tube with tungsten cathode was mounted near the sample holder and operated at 60 kV – 35 mA to measure the X-ray induced radioluminescence spectra.

The crystallographic analyses of grown crystals were performed by powder X-ray diffraction and X-ray rocking curve measurement. The dopant distributions in the crystals were evaluated by energy dispersive X-ray spectrometry. The light yields of scintillators were determined by the pulse height analyses with specially developed VUV-sensitive PMT.

Chapter 3 The radiation imaging detector comprised of MPGD and Nd:LaF$_3$ scintillator

Two-inch diameter Nd^{3+} doped LaF$_3$ single crystals were successfully grown by the Czochralski technique. No remarkable absorption due to unfavorable impurities or color centers was observed from optical absorption measurements in the vacuum ultra-violet spectral region. The high crystallinity and homogeneous Nd^{3+} distribution were found from X-ray rocking curve and chemical composition analysis, respectively. X-ray excited luminescence spectrum was measured and the significant $4f^25d$–$4f^3$ luminescence at 173 nm was observed in the grown crystal. The pulse height spectrum and scintillation decay curve were taken upon γ-ray irradiation. As a result, the grown crystals demonstrated sufficient response to the γ-ray, the light yield of 140 ± 30 photons/MeV, and fast scintillation decay of 7.6 ns.

The Nd:LaF$_3$ crystal was applied to the radiation imaging detector. The MPGD comprised of 2 GEMs and a μ-PIC was used, which can suppress the ion feedback under the high gain operation. The Nd:LaF$_3$ crystal was cut and polished into a piece of 18 mm × 21 mm × 20 mm, and attached on the window of GEM/μ-PIC detector. α-rays from a 3 kBq ^{241}Am source were irradiated to the crystal. The detector was operated at high gain of 6.7×10^5 and the image was successfully obtained. In conclusion, a new type of radiation imaging detector comprised of VUV scintillator and GEM/μ-PIC was successfully demonstrated. However, the light yield of the scintillator should be enhanced toward the practical application.

Chapter 4 Material survey by μ-PD method and evaluation of large size Nd:LiLuF$_4$ single crystal grown by Cz mothod

A material survey was carried out to improve the light yield of the VUV scintillator. Several fluoride crystals doped with Nd or Tm were grown and their luminescence properties were evaluated. Nd:LiLuF$_4$ performed the highest luminescence intensity among the evaluated crystals. The optimum concentration of Nd in LiLuF$_4$ was determined as 1 mol% from the pulse height spectrum measurement.

A Nd:LiLuF$_4$ single crystal of 60 mm in diameter and 45 mm in length was grown by the Czochralski technique. The intense luminescence from the grown crystal peaking at 182 nm has been observed and the intensity was approximately 5 times higher than that of Nd:LaF$_3$. Furthermore, this crystal shows good transparency above 180 nm and no remarkable absorption due to the unfavorable impurities or color centers was observed.

The Nd:LiLuF$_4$ crystal was cut and polished into a disk of φ54 mm × 5 mm, and used for the entrance window of GEM/μ-PIC detector. CsI photocathode was deposited on the inner face of the Nd:LiLuF$_4$. γ-ray from ^{60}Co was collimated by lead block into 5 mm diameter and the radiation images were obtained at several incident points. As a result, the detector of Nd:LiLuF$_4$/MPGD demonstrated position sensitive detection for the high energy γ-ray (1.173 and 1.333 MeV).

Chapter 5 Crystal growth and evaluation of the Nd^{3+} doped LuF_3 single crystals

LuF_3 is a very attractive material for scintillator applications because of its excellent stopping power for high energy photons. The absorption coefficient of LuF_3 for 511 keV γ-ray reaches 0.31 cm^{-1}, and it is comparable with the currently used heavy scintillators such as LSO (0.28 cm^{-1}) or BGO (0.37 cm^{-1}). Furthermore, large band gap of LuF_3 allows scintillation at VUV region that is required in the combination with MPGDs. However, the growth of large size bulk crystals of LuF_3 is difficult because of the phase transition from hexagonal to orthorhombic phases. In order to grow the orthorhombic LuF_3 directly from the melt, top seeded solution growth (TSSG) was applied using LiF as flux. After several attempts, large single crystal of 30 mm in diameter and 30 mm in length was successfully grown. It was free from any visible inclusions or cracks (Fig. 1). The X-ray diffraction pattern of the powdered sample was assigned to orthorhombic structure, and no other impurity phases were detected. The grown Nd:LuF_3 performed intense radioluminescence compared to the other VUV scintillators such as Nd:LaF_3 or Nd:$LiLuF_4$ (Fig. 2). Taking into account this significant luminescence intensity, high density, and large atomic number, Nd:LuF_3 can be considered as the ideal candidate for radiation detectors in combination with MPGDs.

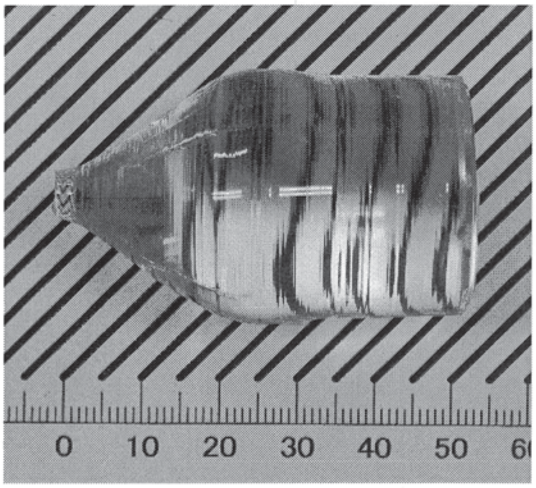

Fig. 1. View of as-grown Nd:LuF_3 single crystal.

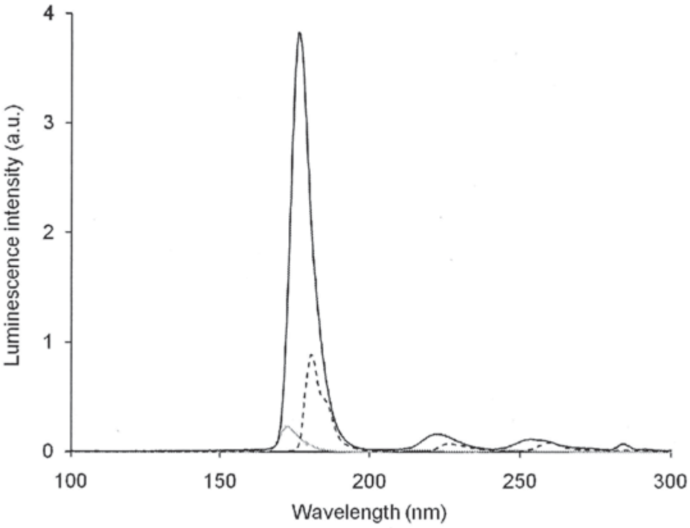

Fig. 2. Radioluminescence spectra of Nd:LuF_3 (solid line), Nd:$LiLuF_4$ (dashed line), and Nd:LaF_3 (gray line).

Conclusions

High quality Nd:LaF_3 single crystal was grown by the Czochralski method and applied to MPGD-based radiation detectors. The detector performance was tested and radiation image was successfully obtained. Several fluoride crystals were grown by the μ-PD method and their scintillation properties were characterized. Among the candidates, Nd:$LiLuF_4$ was found to have a high light yield. A large single crystal of Nd:$LiLuF_4$ was grown by the Czochralski method. Owing the high light yield of Nd:$LiLuF_4$, the radiation detector showed the better performance. A single crystal of Nd:LuF_3 was grown by the TSSG technique using a Czochralski furnace. Along with the potential merit of high density and high Z_{eff}, the Nd:LuF_3 single crystal performed a significant luminescence intensity in VUV region.

論文審査結果の要旨

シンチレーターを用いた放射線検出器は、PET、CT 等の医療分野あるいは手荷物検査等の保安分野等において広く用いられている。近年の放射線利用技術の発展に伴い、放射線検出器にはより高度な性能が求められているが、現在の主流である光電子増倍管を用いた放射線検出器では、位置分解能や製造コストにおいて限界がある。これに対して、ガスカウンタを用いた放射線検出器は位置分解能を飛躍的に向上できるだけでなく、大面積検出器を安価に製作できるという特徴を有する。しかしながら、ガスカウンタ型検出器は、真空紫外で発光するシンチレーターを必要とし、このような短波長域で発光するシンチレーターは稀有であるため、実用化には至っていない。本研究は、ガスカウンタ型検出器の実用化を目指し、真空紫外で発光するフッ化物シンチレーター単結晶の作製と特性評価を行ったもので、全5章からなる。

第1章は、序論であり、本研究の背景と目的を述べている。

第2章では、実験方法を述べている。本研究では、単結晶を迅速に作製することが可能なマイクロ引下げ法（μ-PD 法）を活用して材料探索を行い、有望な材料については、チョクラルスキー法（Cz 法）を用いて大型かつ高品質なバルク単結晶を作製するという一連の材料開発スキームを構築した。また、シンチレーター材料の評価を目的として、真空紫外に対応した X 線励起発光スペクトル測定装置を独自に設計・製作した。

第3章では、Nd:LaF_3 単結晶を用いたガスカウンタ型検出器の実証実験を行っている。Cz 法における結晶作製条件の検討を経て高品質な単結晶の作製に成功し、得られた単結晶をシンチレーターとして用いることにより、ガスカウンタ型検出器が放射線画像検出器として動作可能であることを世界に先駆けて示した。

第4章では、シンチレーターの発光量の向上を目的とした材料探索を行っている。種々の単結晶を作製し、それらの発光特性を評価した結果、優れた発光量を有する Nd:$LuLiF_4$ 単結晶を見出した。

第5章では、さらなる発光量の向上を目的として Nd:LuF_3 単結晶の作製と特性評価を行っている。構造相転移により融液成長が困難とされる LuF_3 の作製に対して Top Seeded Solution Growth 法を適用し、融液からのバルク単結晶の作製に成功した。また、得られた Nd:LuF_3 の発光特性を評価し、当初の Nd:LaF_3 単結晶の 16 倍もの発光強度を有することを明らかにした。

以上、要するに本論文は、真空紫外における発光量に優れたシンチレーター結晶を見出し、大型単結晶の作製技術を確立することによって、ガスカウンタ型検出器の実現可能性を示したもので、次世代放射線検出器の開発ひいては放射線利用技術の発展に寄与するところが少なくない。

よって、本論文は博士(工学)の学位論文として合格と認める。